PATENT SPECIFICATION

(11) 1389 238

(21) Application No. 32582/72 (22) Filed 12 July 1972
(31) Convention Application No. 10479/71 (32) Filed 16 July 1971 in
(33) Switzerland (CH)
(44) Complete Specification published 3 April 1975
(51) INT CL² B01J 13/02 A61J 3/07 A61K 9/50
(52) Index at acceptance
B8C A
A5B 730 734 736 73Y 751 753 756 75Y 764
C3R 1C12 1C15 1C21 1C25 1C6X 1C8P 1C8R 1C9B 1L2C1 1L3A 1L6A 38B2B 38B3C 38B3D 38C10 38C11 38C12 38C13P 38C14B 38C21 38C25 38C26 38C2X 38C33B 38C4 38C6X 38C8P 38C8R 38C9A 38C9B 38C9N 38D2A 38D3A 38D4A 38L2C1 38L3A

(19) THE PATENT OFFICE LONDON

(54) PROCESS FOR ENCAPSULATING OR COATING FINELY DIVIDED MATERIALS BY SPRAY-DRYING-INDUCED POLYMERISATION

(71) We, CIBA-GEIGY AG., a Swiss Body Corporate of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for encapsulating or coating finely-divided materials by spray-drying-induced polymerisation.

The present invention provides a process for encapsulating a substance which is finely distributed in a liquid, by the spray drying process, in which the substance to be encapsulated is finely distributed in a liquid distributing agent containing a reactive surface-active agent obtained from an aminoplast precondensate, said surface-active agent being capable of forming a polymeric product which is insoluble or sparingly soluble in the distributing agent and the preparation thus obtained is subjected to spray drying, such that the reactive surface-active agent polymerises spontaneously, with formation of capsule walls, and dry polymer capsules are obtained.

The reactive system which is based on the surface-active aminoplast can contain one or more such aminoplasts and it can contain other reactive systems such as pheno-plasts. Such systems can, under certain circumstances, for example if the mixture has an acid reaction, and/or is at a high temperature, be converted by polymerisation into an irreversibly insoluble state. Such polymeric products are, in particular, obtained by polycondensation. Since the condensation process is usually completed by the spray drying, it can also be described as "spray condensation".

Suitable reactive systems are formed by the aminoplast precondensates, namely addition products of formaldehyde to nitrogen compounds which can be methylolated (=aminoplast-forming agents). As such aminoplast-forming agents there may be mentioned:

1,3,5 - Aminotriazines such as N - substituted melamines, for example N - butylmelamine, N - trihalogenomelamines, ammeline and guanamines, for example benzoguanamine, acetoguanamine and diguanamines. Further possibilities include alkylureas or arylureas and -thioureas, alkyleneureas or alkylenediureas, for example ethyleneurea, propyleneurea, acetylenediurea or 4,5 - dihydroxyimidazolidone - 2 and derivatives thereof, for example 4,5 - dihydroxyimidazolidone - 2 substituted in the 4-position, at the hydroxyl group, by the radical

$$—CH_2CH_2CO—NH—CH_2—OH.$$

Preferably, the methylol compounds of urea and of melamine are used. In general, products which are as highly methylolated as possible give particularly valuable products. The starting products may be monomolecular or partially pre-condensed compounds. The aminoplast pre-condensates used as starting products for the manufacture of the reactive surface-active agents can also be used in the form of ethers of alkanols with 1 to 3 carbon atoms, especially as methyl ethers.

The manufacture of such aminoplast precondensates is known and, using an aqueous medium, can be effected by, for example, dissolving 1 mol of urea or melamine in an amount of an aqueous approximately 37% strength formaldehyde solution such that 1—3 mols of formaldehyde are present per 1 mol of urea and 3—6 mols of formaldehyde are present per 1 mol of melamine. The solutions thereby produced can optionally be further diluted with water, adjusted to about pH 8

by adding weak bases, for example ammonia solution or triethanolamine, and partially pre-condensed, for example at a temperature from 20°—60°C. Under certain circumstances, these pre-condensates are partially or completely etherified at the methylol groups, for example by alcohols containing at most 3 carbon atoms, in order to improve their solubility in water. The etherification with methanol to give the corresponding methylol-methyl-ethers is of particular interest. The solutions of the pre-condensates, if neutral to slightly alkaline, can be kept for some time if cooled. These aminoplast pre-condensates of low surface actvity can be used by themselves or as a mixture with other reactive systems.

By "surface-active agents" are meant amphiphilic substances which are soluble in water or also in organic solvents, which lower the surface tension of the solvent and which therefore act as emulsifiers or dispersing agents. Molecules of surface-active agents possess both hydrophobic and hydrophilic groups and have the property of accumulating at the phase boundaries (for example oil-water). "Reactive surface-active agents", as used herein, are surface-active agents capable of crosslinking under certain circumstances, preferably if the mixture has an acid reaction or is at a higher temperature, whereby insoluble, resinous condensates are produced which no longer display any surface-active properties. The aminoplasts, preferably urea-formaldehyde or melamine-formaldehyde compounds, which are substituted both by hydrophobic and by hydrophilic groups, are particularly reactive. Such reactive surface-active agents which can be used according to the present invention are known, for example from French Patent Specifications Nos. 1,065,686, 1,381,811, 1,470,103 and 1,581,989.

Such reactive surface-active agents are outstandingly suitable for the manufacture of finely dispersed systems, by which there are to be understood emulsions and dispersions of which the particle diameter of the disperse phase is an average of 1 μ, and preferably even less than 1 μ. If suitably diluted, such dispersions run through ordinary filters and at times even through hardened filters, without leaving a residue. Even substances which are difficult to disperse, such as, for example, viscous adhesive solutions can, in suitable apparatus, be reduced to a very finely distributed form by means of such surface-active agents.

The general property of surface-active agents of accumulating at the phase boundaries, and the special capacity of reactive surface-active agents of crosslinking especially in an acid environment renders the latter suitable for the encapsulating technique.

Particularly suitable reactive surface-active agents are aminoplast pre-condensates containing methylol groups, which additionally contain a) radicals of monohydroxy compounds containing at least 4 carbon atoms and either b_1) radicals of an amine containing hydroxyl groups or b_2) radicals of a polyethylene glycol or b_3) radicals containing at least two alcoholic hydroxyl groups and radicals of the structure Me—O_3S— bonded to carbon atoms, with Me denoting an alkali metal atom, or b_4) radicals of aliphatic hydroxycarboxylic acids which are bonded by the hydroxyl group to the aminoplast pre-condensate, and, optionally, an amine containing hydroxyl groups.

Amongst the aminoplast pre-condensates from which these reactive surface-active agents may be derived, the above-mentioned products which are obtained from formaldehyde and an aminoplast-forming agent are again preferred.

Strongly surface-active etherified methylol-ureas or especially methylolmelamines are preferentially used as reactive surface-active agents.

Amongst the large number of reactive surface-active agents which are suitable for use in the process according to the invention, there are non-ionic, anionic and cationic surface-active agents.

Particularly suitable non-ionic reactive surface-active agents are, for example, curable aminoplast pre-condensates containing etherified methylol groups, the methylol groups of which are at least etherified partly with hydroxy compounds of the formula

$$HO—(CH_2—CH_2—O—)_n—H \qquad (1)$$

wherein n denotes an integer from 2 to 115, and at least partly with a monoalcohol possessing 4 to 7 carbon atoms.

Compounds of the formula (1) are preferably polyethylene glycols. The monoalcohols are, for example, amyl alcohols, hexanol-(1), 2 - ethylbutanol - (1), dodecanol, benzyl alcohol, stearyl alcohol or, above all, n - butanol.

Reactive surface-active agents of particular interest are curable ethers of methylolureas or methylolmelamines, the methylol groups of which are etherified at least partly with a polyethylene glycol of average molecular weight 1,000 to 5,000 and at least partly with an alkanol with 4 to 7 carbon atoms. Reactive surface-active agents of this nature are described in French Patent Specification No. 1,381,811.

Reactive surface-active agents of anionic character which can be used include aminoplast pre-condensates containing etherified methylol groups, the methylol groups of which are reacted at least partly with monohydroxy compounds containing at least 4 carbon atoms and at leastly partly with compounds contain-

ing at least two alcoholic hydroxyl groups, and which contain Me—O_3S— groups bonded to carbon atoms, with Me denoting an alkali metal atom. Me can thus be, for example, a sodium, potassium or lithium atom. Particularly suitable such surface-active agents are above all etherified methylol-ureas or methylolmelamines, the methylol groups of which are etherified at least partly with alkanols which contain 4 to 18 carbon atoms and partly with alcohols of the formula

$$H—(O—CH_2—CH_2)_m—OH$$

wherein m denotes an integer of at most 25, and which contains Me—O_3S— groups bonded to carbon atoms, with Me denoting an alkali metal atom. Such anionic reactive surface-active agents are described in French Patent Specification No. 1,470,103.

Other suitable reactive surface-active agents with anionic character are, for example, aminoplast pre-condensates containing etherified methylol groups, the methylol groups of which are etherified at least partly with monohydroxy compounds which contain 4 to 22 carbon atoms, at least partly with aliphatic hydroxy - carboxylic acids which possess 2 to 4 carbon atoms and optionally, at least partly with an alkanolamine which possesses 2 to 6 carbon atoms. Amongst these reactive surface-active agents, etherified methylol-ureas or methanolmelamines, the methylol groups of which are etherified at least partly with alkanols which contain 4 to 22 carbon atoms, partly with saturated hydroxyalkane-carboxylic acids which possess 2 to 4 carbon atoms and, optionally, partly with ethanolamine, diethanolamine or triethanolamine, are in particular preferred. Such anionic surface-active agents are described in French Patent Specification No. 1,581,989.

As so-colled cationic reactive surface-active agents, aminoplast pre-condensates, the methylol groups of which are reacted at least partly with an alkanol or a fatty acid which each contain at least 4 carbon atoms, and at least partly with an alkanolamine which possesses 2 to 6 carbon atoms, are preferably used. Particularly suitable representatives of such surface-active agents are methylol-melamines, the methylol groups of which are etherified at least partly with an alkanol which possesses 4 to 22 carbon atoms and at least partly with ethanolamine, diethanolamine or triethanolamine. Such cationic reactive surface-active agents are described in French Patent Specification No. 1,065,686.

Further, as already mentioned, so-called phenoplast pre-condensates can be used with the aminoplasts to form the reactive system. These are phenol-aldheyde, especially phenol-formaldehyde, pre-condensates. As the phenol it is possible to use, in particular, phenol itself, and also substituted phenols such as *o*-, *p*- or *m*-cresol.

In the process according to the present invention, the conversion of the reactive surface-active agents derived from the aminoplast precondensates into the irreversibly insoluble state can be initiated, and completed, by various measures, in particular by raising the temperature, establishing certain pH values, adding substances which react with the surface-active agents (or aminoplast pre-condensates) to form high molecular products, and especially by adding so-called "curing" catalysts which have an acid reaction.

Where encapsulation is carried out in an aqueous medium, the pH value of the preparation is preferably 2 to 5. Suitable substances for adjusting the pH value are above all aliphatic carboxylic acids which are less volatile than the distributing agent, for example citric acid, or inorganic acids, such as hydrochloric acid or phosphoric acid, and also acid or hydrolysable salts such as aluminium sulphate, titanium oxychloride, magnesium chloride and ammonium salts of strong acids, such as ammonium chloride, ammonium nitrate, ammonium sulphate or ammonium dihydrogen phosphate. It is also possible to use oxidising agents which are capable of oxidising formaldehyde to formic acid, such as hydrogen peroxide. However, the use of acids has proved most appropriate.

The amounts used of the reactive system and of the substance to be encapsulated can be very different, depending on the end use of the capsules and the nature of the substance to be encapsulated. To encapsulate liquid substances it has proved appropriate to employ generally 5 to 100 parts by weight of the component of the reactive system per 100 parts by weight of liquid. In the case of solid substances to be encapsulated, the lower limits of these amounts to be used are, as a rule, somewhat higher, that is to say, for example, 30 to 100 parts by weight of the components of the reactive system are used per 100 parts by weight of solid substance. The parts by weight in the case of the reactive system here naturally relate to the dry product.

As already mentioned, water is preferably used as the distributing agent, and a substance which is insoluble or only sparingly soluble in water and does not react with water is used as the finely distributed substance. However, it is also possible to use organic solvents which are immiscible with water as the distributing agent and water-soluble substances or aqueous solutions thereof as the finely divided substance.

As examples of such distributing agents there may be mentioned aliphatic or aromatic hydrocarbons and halogenated hydrocarbons such as benzene, toluene, chlorobenzene, tetra-

hydronaphthalene and decahydronaphthalene, trichloroethylene or carbon tetrachloride.

The proportion of encapsulated substance relative to the total capsule composition can vary greatly. It can be as little as, for example, 20 per cent by weight, or up to 99 per cent by weight. Preferably, however, it is 50 to 95 per cent by weight. Depending on the end use, the thickness of the walls of the capsules can be varied. The walls can thus be made hard or flexible. The degree of porosity of the capsule walls can in this way also be adjusted as desired.

The reactive compounds mentioned can be used by themselves, or in mixtures, for the encapsulation. Physical mixtures can be used, that is to say mixtures of different pre-condensates or reactive surface-active agents or mixtures of pre-condensates with reactive surface-active agents. However, according to the invention it is also possible to use chemical mixtures, that is to say pre-condensates or reactive surface-active agents which are manufactured from mixtures of different aminoplast-forming agents.

The dispersing, in the distributing agent, of the substance to be encapsulated, which is necessary before encapsulation, is advantageously effected by the addition of reactive surface-active agent to the distributing agent. The advantage of the use of the reactive surface-active agent is that during the encapsulation effected by spray drying it loses its surface-active character and as a result of the polycondensation becomes a constituent of the shell. Mixtures of non-surface-active reactive pre-condensates with small proportions of reactive surface-active agents are particularly suitable according to the invention. Mixtures of 5—20 parts by weight of a non-surface-active pre-condensate with 1 part by weight of reactive surface-active agent are particularly advantageous.

The preparations envisaged for spray drying, which, according to the invention, contain a reactive system, a distributing agent and a substance to be encapsulated, can contain further auxiliaries and additives in addition to an auxiliary which can be condensed.

Thus, for example, protective colloids and thickeners which are soluble in the distributing agent can be added. These substances can firstly influence the viscosity of the emulsions and suspensions provided for spray drying and can thereby influence the particle size of the capsules and microcapsules formed during spray drying. Secondly, they can influence the quality of the shells of the condensed reactive systems in that they form, together with these, a mutually inter-penetrating lattice. In a solvent, for example water, a protective colloid or thickener soluble therein is dissolved out of the capsule wall. The mechanical properties and permeability of the shells which result therefrom depend on the proportion of the protective colloid or thickener in the shell. As auxiliaries in this sense it is possible to use, for example, methylcellulose, hydroxypropylcellulose, soluble starch, gum arabic and polyvinylpyrrolidone.

In order to disperse the material to be encapsulated in the distributing agent it is possible also to add non-reactive surface-active substances in addition to the reactive surface-active agents. The former can be both ionic or non-ionic in character. These substances form a constituent of the shell after encapsulation and therefore improve the wettability of the particles and, under certain circumstances, the permeability of the shells, if the capsules are re-dispersed in a solvent, for example water.

When encapsulating active substances of high activity, these substances can be mixed with disperse fillers, applied to these fillers, for example by granulation, or absored on these fillers. The fillers may be organic or inorganic, mostly inert, substances, for example starch, highly disperse cellulose derivatives, bentonite, kaolin, gypsum and silica.

It is also possible to add, as auxiliaries, plasticisers, for example, which are soluble in the distributing agent such as, for example, lactose, sucrose or organic and inorganic salts.

The substances which can be finely distributed in accordance with the process of the present invention may be solid or liquid.

Solids are preferably dispersed in the presence of a reactive surface-active agent and, if necessary, are comminuted by grinding in such a way as to produce a stable dispersion.

If the substance to be encapsulated, that is to say the inner phase, is a liquid, it must not be soluble in the distributing agent, that is to say in the outer phase, or must at least not be miscible therewith. In general, the outer and the inner phase should be so chosen that neither significant amounts of one phase are dissolved by the other nor undesired chemical reactions take place. As dispersed solids it is possible to use the most diverse active substances, such as pigments, fillers, pesticides, scents, fats, waxes, paraffin, fertilisers or pharmaceuticals. Possible liquid substances to be emulsified are undiluted liquid active substances, such as, for example, paraffin oil, or solutions of liquid or solid active substances in suitable solvents. In general, liquid substances which have a high boiling point or are of low volatility are preferred. As examples, phthalic acid dibutyl ester and phosphoric acid tricresyl ester, and chlorinated diphenyl, may be mentioned here. Furthermore, other water-insoluble solvents, the volatility of which is more pronounced, such as, for example, petroleum, toluene or xylene, can also be used. Organic solvents which are sparingly soluble in water can thus, in the present process, be used in two different ways,

firstly as a distributing agent for an aqueous inner phase (water-in-oil emulsion) and secondly as an inner phase, in which case they, in general, additionally contain at least one further substance, for example a fatty dyestuff, a dyestuff precursor or an adhesive, in solution (oil-in-water emulsion). Equally, water or aqueous solutions can be used as the outer or as the inner phase. Salts, dyestuffs or adhesives can, for example, be dissolved in an inner aqueous phase. The situation can also arise, such as, say, in the case of fats, waxes or paraffins, that the inner phase which is formed by these substances is first liquid because of the higher working temperature, so that an emulsion is present, and this changes to the solid state on cooling. Similarly, dissolved substances can crystallise, within the capsules, out of aqueous solutions which are emulsified in a non-aqueous outer phase, during the process or subsequently.

Spray drying, also called atomising drying, is in itself known and in order to carry out the process according to the invention it is possible to use the customary spray drying apparatuses, that is to say, for example, a disc, propellor or jet atomiser (compare, for example, " Seifen-Oele-Fette-Wachse " 1961, pages 750—752 and 794—795 or " Soap and Chemical Specialties ", February 1962, pages 147—149 and 157, or Römpp, Chemie-Lexikon (Chemical Encyclopaedia), 6th Edition, 1966, Volume III).

Preferably, the spray drying is carried out at temperatures of 50 to 250°C, especially 50 to 200°C, in a stream of gas, with nitrogen, carbon dioxide or, especially, air being used as the gas.

The deciding factor regarding the temperature to be used is the boiling point of the distributing agent, in that it is of course advantageous to carry out the spraying above the boiling point of the distributing agent. Furthermore, the heat stability of the substance to be encapsulated is also of considerable importance.

Preferably, a disc turbine atomiser which executes 5,000 to 40,000 revolutions per minute is used.

The advantages of the process according to the invention over known processes wherein polymer preparations are spray-dried are based, in particular, on the fact that, for example, lyophilic systems can, simultaneously, that is to say in one process step, be sprayed or dispersed, polymerised and dried. This technical advantage of course has economic advantages.

Since, during spray drying, the preparation containing the reactive system is heated up very rapidly, the almost instantaneous temperature rise resulting therefrom causes an immediate polymerisation of the reactive system. As a result of this rapid heating and the immediate increase in surface area during spraying, very favourable heat transfer conditions also prevail in the process according to the invention, which also accelerate the polymerisation. The rapid withdrawal of volatile products (for example water or formaldehyde) during the polymerisation whilst spraying also accelerates the reaction.

Spraying by means of jets under high pressure and by means of disc atomisers or high speed propellors causes an additional dispersion and at the same time prevents secondary agglomeration of the disperse phase during the very brief polymerisation and drying process.

The suspensions or emulsions intended for encapsulation first undergo very fine distribution during spray drying. The finest and most uniform distribution can generally be achieved when using disc turbine atomisers. The viscosity of the distributing liquid should as a rule be so chosen that the liquid film adhering to these liquid or solid particles is not torn off the particles as a result of the high relative speed and the edge of the disc but is retained on the surface of the particles and is condensed there. If the liquid film is torn off, the reactive system condenses in isolated small droplets but it is not utilised for the encapsulation. Given a suitable relationship between the viscosity of the distributing liquid and the speed of rotation of the disc atomiser, droplets are formed which keep the core materials completely enclosed individually or in agglomerates. During the subsequent polycondensation of the shells, crosslinking produces an insoluble, dense structure which possesses the external shape of the droplets formed during spraying, and completely encloses the core particles.

When encapsulating liquid substances, in particular, the capsules have to meet more stringent requirements, in order to prevent the shells breaking, than when encapsulating solid substances which in themselves already ensure a certain mechanical strength. In the case of liquid core materials the proportion of shell materials will therefore generally have to be greater than when encapsulating solid substances.

By selecting the dispersing conditions and spray conditions, it is possible to manufacture primary capsules of almost any desired particle size, which have not stuck together to form secondary agglomerates.

As a rule, the diameter of these capsules or micro-capsules is 0.1 to 100 μ and at times several μ, preferably 1 to 50 μ or especially 10 to 30 μ.

The dry capsules are a fine, free-flowing powder. They can furthermore be used as a suspension in a liquid, as shaped articles, pressed into tablets, as a surface coating or in any other form in which the capsules are preserved as such.

The capsules can be kept for a very long

time. Even temperatures of about 100°C generally do not interfere with the quality of the capsules provided no heat-sensitive substances have been encapsulated.

The encapsulated finely divided substance can be liberated in various ways from the capsules. As a rule, this is done mechanically by fracturing the capsule wall by applying pressure thereto. Furthermore, the substance, above all if it is not liquid, can also be liberated by dissloving away the capsule wall by means of a suitable solvent, or by shear forces, friction, heat, ultrasonics, enzymes or slow diffusion through a partially intact capsule wall.

The capsules manufactured according to the invention can be employed in the whole field of use of micro-capsules, that is to say, for example, wherever separation from the reactive material is desired, where active substances are not to become active immediately but are to undergo controlled release and where liquids are to be converted into solid forms, where odours are to be masked. For example, it is possible to encapsulate adhesives, agricultural chemicals such as agents for combating harmful organisms, for example herbicides, pesticides or fungicides or fertilisers, flavouring substances, dyestuff solutions, dyestuff precursors solutions, fuels, oils, catalysts, scents, cleansing agents and the like. Such uses and others are described, for example, in Kirk-Othmer, Encylopedia of Chemical Technology, Vol. 13, 2nd Edition 1967 in the chapter "Micro-encapsulations" by J. A. Herbig.

The capsules manufactured according to the process of the invention are in particular also suitable for the manufacture of pressure-sensitive copying papers. Herein, dyestuff precursors, optionally together with antioxidants or UV-absorbers, are encapsulated and applied to the papers or incorporated into the paper pulp. The dyestuff precursors, as a rule encapsulated as an organic solution, can be applied, for example to the rear of a paper. The capsules are burst by pressure and the dyestuff precursor solution is transferred image-wise to the top surface of a paper underneath it, which is coated with a developer. This process is also called the "Chemical Transfer" process.

In the so-called "Chemical-Self-Contained" process, the encapsulated dyestuff precursor and the developer are applied in one layer to the paper, so that the top face of each sheet is permanently active. In the case of so-called "Monoform" papers, the capsules and the developer have together been incorporated into the paper pulp.

Kaolins which give an acid reaction can be used, for example, as developers.

Such papers coated with the capsules manufactured according to the invention possess excellent storage stability. After a storage of over 10 hours at 100°C, unchanged good copies with sharp, non-smudged script edges can be obtained.

In the Manufacturing Instructions and Examples which follow, and which further illustrate the present invention, parts and percentages are by weight.

Manufacturing Instructions for Reactive Surface-Active Agents

1. 206 parts of 36.5% strength aqueous formaldehyde, 170 parts of n-butanol and 60 parts of urea are treated with 8 parts of 25% strength ammonia and heated in a stirred flask, with descending condenser, to 96°C for 2 hours, in the course of which a total of 32 parts of n-butanol-water mixture distil off. The mixture is now cooled to about 50°C and 1 part of 85% strength phosphoric acid dissolved in 20 parts of n-butanol is added. The whole is now heated in vacuo to 80°C, in the course of which water and n-butanol distil off. The water is separated from the distillate whilst the n-butanol runs back again into the reaction vessel. After 4 hours, the product is practically free of water and is miscible with benzene in any ratio. It is now neutralised by adding 5 parts of triethanolamine and evaporated in vacuo to 212 parts, whereby the product subsequently described as lacquer resin A is obtained.

212 parts of the urea - formaldehyde - butanol lacquer resin A (corresponding to 1 mol or urea) together with 177 parts of polyethylene glycol of average molecular weight 1,540 are heated to 120—130°C until the product has become water-soluble to give a clear solution, during which about 24 parts of butanol distil off. 35 parts of triethanolamine are now added and the mixture is further heated to 120°C over the course of one hour.

The resulting condensation product is treated with sufficient distilled water to give a 50% strength slightly yellowish clear solution which can be further diluted with water to any desired extent. The product proves an excellent emulsifier in alkaline (pH=9.0) or in weakly acid solution (pH=5.0) and is crosslinked by strong acid, especially at a elevated temperature. 100 parts of 50% strength surface-active agent solution give about 6 parts of insoluble resin.

II. 390 parts of hexamethylolmelamine - hexamethyl - ether, corresponding to 1 mol of melamine, are heated with 372 parts (2 mols) of dodecanol and 1,540 parts (1 mol) of polyethylene glycol of average molecular weight 1,540, in the presence of 3.35 parts of 85% strength phosphoric acid, to 115—130°C for one hour, in the course of which 97 parts of methanol distil off. The reaction product is neutralised with 10 parts of triethanolamine. A waxy, easily water-soluble surface-active agent is obtained. Its aqueous

solutions foam and show an excellent emulsifying and dispersing action.

III. 212 parts of the urea - formaldehyde - butanol lacquer resin A described in Instruction I (corresponding to 1 mol of urea) are heated with 70 parts of glycollic acid butyl ester and 4 parts of glacial acetic acid in vacuo to 85—90°C, until 42 parts of n-butanol have distilled off. The mixture is then stirred for a further hour at 100°C under reflux. Finally, the reaction product is diluted with 140 pars of ethanol, 35 parts of solid potassium hydroxide are added and the mixture is heated under reflux for 15 minutes, in the course of which the ester groups are saponified. After evaporation in vacuo, 225 parts of a solid, slightly brownish, easily water-soluble substance are obtained. If a little acid is added to the strongly foaming solution, a crosslinked product which is insoluble in alkali precipitates.

IV. 126 parts of melamine, with the addition of 18 parts of 25% strength ammonia, are dissolved in 590 parts of 36.5% strength aqueous formaldehyde, containing methanol, at 60°C. The mixture is warmed to 80°C and over the course of about 20 minutes 132 parts of a mixture of methanol and water are distilled off in vacuo. 490 parts of n-butanol are now added and distillation in vacuo is continued, whilst separating the water - n - butanol mixture which passes over. The n-butanol runs back again into the reaction vessel whilst 118 parts of an aqueous layer separate out. 3 parts of 85% strength formic acid, dissolved in 5 parts of n-butanol, are added and now a total of 452 parts of n-butanol is distilled off, carrying with it the last traces of water. 532 parts of a viscous colourless resin which is miscible with benzene in any desired ratio and is subsequently described as lacquer resin B are obtained.

532 parts of the melamine - n - butanol lacquer resin B (containing 1 mol of melamine) and 104 parts of triethanolamine are heated, whilst stirring, to 120°C over the course of 1½ hours and then to 125—140°C over the course of 1½ hours, during which 76 parts of n-butanol distil off. After cooling, 560 parts of a clear, viscous product which is easily soluble in 10% strength acetic acid are obtained. Its acid solutions show an excellent emulsifying capacity. At a pH value of 4.0 and slightly raised temperature an insoluble resin is formed. These properties characterise the product as a reactive surface-active agent. The product has a solids content of 80 to 85%. In 5% strength aqueous solution this reactive surface-active agent causes a lowering of the surface tension of water from 72.75 dyn/cm to 37.6 dyn/cm.

V. 445 parts of the lacquer resin B from Instruction IV are mixed with 50 parts of a polyethylene glycol of average molecular weight 4,000. The mixture is warmed to 95—100°C and 3 parts of glacial acetic acid are added. Heating to 95—100°C is continued until a sample of the reaction product gives a clear solution in water. 70 parts of tri-alkanolamine are now added and the mixture is stirred and warmed to 120°C for a further 2 hours. After cooling, a colourless, waxy substance which is easily miscible with water at 60°C is obtained. Addition of the same amount of water and of a little acetic acid yields a 50% strength slightly turbid solution of surface-active agent of pH value 8.1 to 8.2. In 5% strength aqueous solutions this reactive surface-active agent lowers the surface tension of water from 72.75 dyn/cm to 41.0 dyn/cm.

Example 1

A homogeneous supension is manufactured from 400 g of a 1% strength low viscosity methylcellulose hydrogel and 100 g of 5 - allyl - 5 - isobutyl barbituric acid of average particle size up to 20 μ, by vigorous stirring by means of a high speed stirrer.

20 g of a 50% strength solution of a reactive surface-active agent (according to Instruction I) are added to this suspension. Thereafter, the suspension is acidified to pH 2.5 with saturated citric acid solution or 6 N phosphoric acid.

Thereafter, the suspension is immediately passed into a disc atomiser for spray drying (between 30,000 and 40,000 revolutions/minute). The air input temperature is about 200°C and the output temperature about 100—105°C.

105 g of a free-flowing powder are obtained.

The individual units of this powder consist of a core of 5 - allyl - 5 - isobutyl barbituric acid particles which is surrounded by a shell of the reactive surface-active agent I which has now been polycondensed. The capsule wall also contains a proportion of methylcellulose.

After prolonged elution in aqueous solutions of the micro-capsules thus manufactured, the polycondensed reactive surface-active agent is left in the form of a finely structured intact shell which is soluble in aqueous solutions.

Instead of the reactive surface-active agent I, one of the reactive surface-active agents II to V can be used with comparable success.

Example 2

125 g of a 4% strength methylcellulose hydrogel (medium viscosity) and 10 g of highly disperse silica are added to 50 g of a 3% strength polyoxyethylene - sorbitane - laurate solution whilst stirring with a high speed stirrer. This mixture is introduced, with vigorous stirring, into 50 g of paraffin oil (medium viscosity) and the whole is made up with water to 500 g, whereupon an oil-water emulsion-suspension is obtained.

450 g of the emulsion thus produced are mixed with 50 g of a 50% strength solution of the reactive surface-active agent I and the mixture is acidified to pH 2.5 with saturated citric acid solution or 6 N phosphoric acid.

Thereafter this emulsion is immediately spray-dried as described in Example 1.

About 60 g of a white powder are obtained. The individual units of the powder consist of paraffin droplets which are encapsulated with a shell of polycondensed reactive surface-active agent, with the capsule walls additionally containing proportions of methylcellulose and silica.

Example 3

A homogeneous supension is manufactured from 400 g of a 1% strength low viscosity hydroxypropylmethylcellulose hydrogel (50 Cps) and 100 g of 5 - allyl - 5 - isobutyl barbituric acid of average particle size about 20 μ, by intensive stirring by means of a high speed stirrer. 5 g of a 50% strength solution of a reactive surface-active agent (according to Instruction II) and 70 g of a 50% strength aqueous solution of a melamine - formaldehyde precondensate are added to the suspension. Resulting suspension is again homogenised by means of a high speed stirrer and is thereafter acidified with saturated tartaric acid solution to pH 3.8, after which it is immediately spray-dried, with slight stirring, in a spray drier equipped with a high speed disc atomiser, at 30,000—40,000 revolutions/minute. The air input temperature is 200°C and the output temperature 90—105°C. 115 g of a free-flowing powder are thus obtained. The particles have an average particle size of 30—40 μ and consist of a core of barbituric acid particles which are surrounded by a shell of insoluble melamine - formaldehyde condensate and methylcellulose constituents. The powder can be converted into medicinal forms with long-lasting release of the active substance.

Example 4

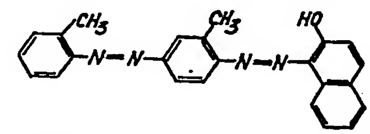
Example 3 can, with comparable success, be carried out by employing corresponding amounts of a urea-formaldehyde precondensate and a reactive surface-active agent according to Instruction II.

Example 5

A precondensate is manufactured from a solution of 25 g of purified acid casein, 20 g of urea, 5 g of thiourea, 3 g of sodium tetraborate, 127 g of water and 50 g of 37% strength aqueous formaldehyde solution by letting the solution stand for 12 hours at room temperature. Hereupon it assumes a pH value of 5.6. It is subsequently diluted with 464 g of water. A mixture of 90 g of chlorinated diphenyl and 90 g of paraffin oil, in which 3.6 g of crystal violet lactone and 2.4 g of benzoyl-leuco methylene blue are dissolved, is emulsified by means of a high speed stirrer in the solution of the precondensate and the mixture is subsequently acidified to pH 4 and spray-dried in the usual manner by means of a disc atomiser (air input 180°C, air output 95°C). An almost colorless, fine dry powder is obtained, which when crushed on a paper coated with an acid developer instantaneously produces blue colour effects. The capsule powder is therefore suitable for the manufacture of pressure-sensitive copying papers.

Example 6

100 g of thin paraffin oil which is dyed with the dyestuff of the formula (2)



are emulsified by means of a suitable stirrer in a solution of 40 g of a reactive surface-active agent according to Instruction IV. A solution of 20 g of polyvinylpyrrolidone of medium viscosity and 40 g of hexamethylolmelamine - hexamethyl - ether in 100 g of water is mixed into this emulsion. The emulsion is acidified to pH 3.5 with saturated citric acid solution and is spray-dried, with further stirring, in a spray drier at an air input temperature of 200°C and an output temperature of 95°C. 110 g of a free-flowing dry powder can thereby be obtained, consisting of capsules of average particle size about 20 μ which contain dyed paraffin oil. On crushing the capsules, for example on paper, they produce red colour effects.

Example 7

200 g of finely ground kaolin of average particle size 10 μ together with 60 g of a 5% strength solution of 2,4 - dichlorophenoxyacetic acid in ethanol are granulated and dried. The compositions obtained after drying are again comminuted, by grinding, to an average particle size of 10—20 μ and suspended in 800 g of a 20% strength aqueous solution of a melamine - formaldehyde precondensate. 20 g of polyvinylpyrrolidone of medium viscosity are added to the solution. The suspension thereafter obtained is spray-dried in the usual manner after having been acidified to pH 3.8 with aqueous tartaric acid solution. The powder thereby produced is a herbicide which is difficult to elute and is therefore active for a long time. It has an average particle size of 30—40 μ.

The ease of elution of the active principle can be controlled somewhat by varying the amount of added protective colloid, with the ease of elution increasing with increasing amount.

Example 8

Insecticides of longer-lasting effect and of reduced ease of elution can be manufactured in the same manner as indicated in Example 8 by impregnating kaolin with phosphoric acid esters and other insecticidally active compounds (chlorinated compounds) and subsequent encapsulation.

Example 9

6 g of highly disperse silica are suspended in 400 g of a solution of 5 g of polyvinylpyrrolidone - vinyl acetate copolymer of medium viscosity, 6 g of lactose, 6 g of polyethylene oxide - sorbitane - oleate and 100 g of a curable phenol - formaldehyde precondensate. 50 g of toluene in which 5 g of butyl rubber are dissolved, are emulsified in this suspension by means of a high speed stirrer. This is done at a pH of 7.8. The emulsion is acidified to pH 3 with 6 N phosphoric acid whilst stirring continuously and is subjected to spray condensation in the usual manner whilst continuing to stir in order to maintain the homogeneity. A dry powder is obtained, which contains butyl rubber dissolved in toluene. If a slight pressure is exerted on the capsules the contents exude, with the solvent evaporating. The powder is thus a dry adhesive which can be activated by pressure.

Example 10

10 g of highly disperse silica and 5 g of lactose are dispersed, or dissolved, in 400 g of an 0.5% strength aqueous solution of a polyvinylpyrrolidone - vinyl acetate copolymer. 20 g of a 50% strength solution in water of a reactive surface-active agent according to Instruction V and 50 g of hexamethylolmelamine - trimethyl - ether are added to the solution, which is homogenised by stirring. 55 g of toluene are emulsified in the solution by high speed stirring. The emulsion is acidified to pH 3 with 6 N phosphoric acid whilst continuing to stir and is spray-dried in the usual manner (input temperature 180°C, output temperature 85°C). When subjected to pressure, the dry powder thereby obtained releases toluene, the shells being destroyed. It is therefore a dry spot remover which is easy to handle.

Example 11

10 g of lactose, 5 g of glycerine, 40 g of a urea-formaldehyde precondensate and 20 g of hexamethylolmelamine - hexamethyl - ether are dissolved in 500 g of a 1% strength aqueous solution of methylcellulose of medium viscosity, by stirring. 60 g of olive oil are emulsified therein, by means of a suitable stirrer, in such a way as to give an average particle size of approx. 10 μ. Amounts of saturated citric acid solution which serve to establish a pH of 3.5—4 are added whilst continuing to stir. Immediately thereafter, the emulsion is spray-dried in the manner described. A dry powder which contains encapsulated olive oil is obtained. Olive oil encapsulated in this way can be packaged in paper.

Example 12

Instead of olive oil it is also possible to encapsulate, for example, oleic acid by the same procedure as in Example 12. Encapsulated oleic acid is suitable for use as an additive to cosmetic preparations (paste, powders and creams). The content of the capsules can be released by, for example, massaging into the skin.

Example 13

5 g of a reactive surface-active agent according to Instruction I and 60 g of hexamethylolmelamine - hexamethyl - ether are dissolved in 500 g of an aqueous solution which contains 100 g of a 50% strength solution of a melamine - formaldehyde precondensate. 100 g of machine oil of medium viscosity are emulsified in the resulting solution, by means of a high speed stirrer, until an average particle size of approx. 10 μ is obtained, and the emulsion is diluted with 300 g of water. Thereafter it is acidified to pH 3.5 with 6 N phosphoric acid and spray-dried in the usual manner. The resulting mass is of solid consistency and under mechanical load exhibitis waxy properties. It can be used as a solid lubricant.

Example 14

10 g of polyvinylpyrrolidone - vinyl acetate copolymer of medium viscosity, 10 g of finely disperse silica, 8 g of lactose and, as reactive systems, 100 g of an ethyleneurea - formaldehyde pre-condensate and 10 g of a 50% strength aqueous reactive surface-active agent solution according to Instruction I, are dissolved or dispersed in 500 g of water. 80 g of pine oil are emulsified in this solution by means of a stirrer in such a way as to give an average particle size of less than 5 μ. The emulsion is acidified to pH 4 with citric acid solution, whilst continuing to stir, and is spray-dried with the aid of a disc atomiser. The resulting dry powder contains encapsulated pine oil and can be used for conferring an aroma, and as a scent correctant.

WHAT WE CLAIM IS:—

1. Process for encapsulating a substance which is finely distributed in a liquid which comprises finely distributing the substance to be encapsulated in a liquid distributing agent containing a reactive surface-active agent obtained from an aminoplast pre-condensate, said surface-active agent being capable of forming a polymeric product which is insoluble or sparingly soluble in the distributing agent, and spray drying the resulting liquid

under conditions such that the reactive surface-active agent polymerises spontaneously to form capsule walls giving dry polymer capsules.

2. Process according to claim 1 wherein the distributing agent also contains an aminoplast pre-condensate which is not a surface-active agent and is capable of forming a polymeric product which is insoluble or sparingly soluble in the distributing agent.

3. Process according to claim 1 or 2 wherein the aminoplast which forms a reactive surface-active agent is a methylolmelamine and/or methylolurea, which is not etherified or is etherified with an alcohol containing at most 3 carbon atoms.

4. Process according to claim 3, wherein the aminoplast is a dimethylolmelamine to hexamethylolmelamine.

5. Process according to claim 3, wherein the aminoplast is a urea - formaldehyde pre-condensate.

6. Process according to any one of the preceding claims wherein the reactive surface-active agent is an aminoplast pre-condensate containing methylol groups, and at least one of (a) a monohydroxy radical containing at least 4 carbon atoms, and either (b_1) an amino radical containing at least one hydroxyl group, or (b_2) a radical of a polyethylene glycol or (b_3) a radical containing at least two alcoholic hydroxyl groups and $Me—O_3—S—$ groups bonded to carbon atoms, with Me denoting an alkali metal atom or (b_4) an aliphatic hydroxycarboxylic acid radical which is bonded to the aminoplast precondensate by the hydroxyl group, and, optionally, an amine containing at least one hydroxyl group.

7. Process according to claim 6 wherein the reactive surface-active agent is a surface-active etherified methylol - melamine or methylolurea.

8. Process according to claim 6 or 7 wherein the reactive surface-active agent is an aminoplast pre-condensate, containing etherified methylol groups, the methylol groups of which are at least partly etherified with hydroxy compounds of the formula:

$$HO—(CH_2—CH_2—O)_n—H$$

wherein n denotes an integer from 2 to 115, and at least partly with a mono-alcohol possessing 4 to 7 carbon atoms.

9. Process according to claim 8, wherein the reactive surface-active agent is a curable ether of a methylolurea or methylolmelamine, the methylol groups of which are etherified with an alkanol which contains 4 to 7 carbon atoms and with a polyethylene glycol of average molecular weight 1,000 to 5,000.

10. Process according to claim 6 or 7 wherein the reactive surface-active agent is an aminoplast pre-condensate containing etherified methylol groups, the methylol groups of which are reacted at least partly with monohydroxy compounds containing at least 4 carbon atoms and at least partly with alcohols containing at least two hydroxyl groups, and which contain $Me—O_3S—$ groups bonded to carbon atoms, with Me denoting an alkali metal atom.

11. Process according to claim 6 or 7 wherein the reactive surface-active agent is aminoplast pre-condensate containing etherified methylol groups, the methylol groups of which are reacted at least partly with a monohydroxy compound which contains 4 to 22 carbon atoms, at least partly with an aliphatic hydroxycarboxylic acid which contains 2 to 4 carbon atoms and, optionally, at least partly with an alkanolamine which possesses 2 to 6 carbon atoms.

12. Process according to claim 6 or 7 wherein the reactive surface-active agent is an aminoplast pre-condensate, the methylol groups of which are reacted at least partly with an alkanol or a fatty acid, each of which contain at least 4 carbon atoms, and at least partly with an alkanolamine which possesses 2 to 6 carbon atoms.

13. Process according to claim 12 wherein the reactive surface-active agent is a methylolmelamine, the methylol groups of which are etherified at least partly with an alkanol which possesses 4 to 22 carbon atoms and at least partly with ethanolamine, diethanolamine or triethanolamine.

14. Process according to any one of the preceding claims wherein the reactive surface-active agent is converted into the irreversibly insoluble state by addition of acid.

15. Process according to any one of the preceding claims wherein water is used as the distributing agent and a substance which is insoluble in water and does not react with water is used as the finely distributed substance.

16. Process according to any one of claims 1 to 14, wherein an organic solvent which is immiscible with water is used as the distributing agent and a water-soluble substance or aqueous solution thereof is used as the finely divided substance.

17. Process according to any one of the preceding claims wherein the spray drying is carried out at 50° to 250°C.

18. Process according to any one of claims 1 to 16 wherein a disc, propeller or jet atomiser is used.

19. Process according to any one of claims 1 to 16 and 18 wherein spray drying is carried out in a warm stream of air.

20. Process according to any one of the preceding claims wherein the substance to be encapsulated is a water-insoluble solvent, pesticide, dyestuff solution, dyestuff precursor solution, medicine, adhesive, fertiliser, fuel, oil, scent, catalyst, cleansing agent or flavouring substance.

21. Process according to claim 1 substantially as hereinbefore described.

22. Process according to claim 1 substantially as described in any one of Examples 1 to 14.

23. A substance whenever encapsulated by a process as claimed in any one of claims 1 to 20.

24. A pressure-sensitive copying material containing an encapsulated dye, or dye precursor, as claimed in claim 23.

25. A substance whenever encapsulated by a process as claimed in claim 21 or 22.

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square,
Gray's Inn,
London, WC1R 5EU.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.